DRAFT
Protocol for Assessing the Ozone Impact of Permeation VOCs Relative to Carbon Monoxide

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The purpose of this paper is to discuss a modeling approach for assessing the potential air quality impacts associated with the use of ethanol in gasoline. Specifically, the objective of the approach is to characterize the net impact of increased permeation VOC emissions relative to reduced CO emissions. This paper will describe the problem to be addressed, previous related work, a modeling approach, and the expected results.

PROBLEM:

A recent CRC study indicates that, on average, the permeation VOC increase of ethanol fuel (5.7% ethanol) is about 1.11 g/veh/day compared to non-oxygenate fuel while the CO exhaust emissions decrease by about 7.8 g/veh/day statewide in 2004 according to EMFAC2002 (ver. 2.2, April 23, 2003). In other words, CO mass reduction is approximately 7 times that of the permeation VOC increase. It is therefore argued that ozone reductions can be achieved by adding ethanol into gasoline because of the significant reduction of CO emissions.

PREVIOUS WORK:

A preliminary reactivity analysis has been conducted to assess the ozone impact of permeation VOCs relative to CO and is briefly described here. Several reactivity scales derived from either box-model (e.g., MIR and MOIR) or 3-d model (e.g., regional-MIR) for both 1-hr and 8-hr impacts were used to characterize the ozone impact of ethanol fuel. 3-D model-derived scales also include those conducted for other regions such as the Eastern United States in addition to California areas. For this analysis, we compared the reactivity of CO with the top 7 permeation VOCs representing over 60 percent of total permeation VOCs in terms of mass and MIR reactivity. Below is a summary of our key findings.

- CO has a MIR of 0.06 while the permeation VOC emissions have a composite MIR of 3.27. The difference indicates that one ton of permeation VOC is **55** times as effective as one ton of CO emissions (3.27/0.06) in terms of ozone formation.
- Reactivity analyses using reactivity scales other than MIR indicates that one ton of permeation VOC is in the range of **34 to 59** times as effective at ozone formation as one ton of CO emissions using metrics for California and is about 20 times as effective at ozone formation using metrics derived for the

Eastern United States. The difference is expected since California urban areas are more sensitive to VOC emissions (VOC-limited), i.e., MIR-like conditions than the Eastern US regions.

OBJECTIVE:

The remainder of this document describes an approach for characterizing the ozone impact of permeation VOCs relative to CO emissions using an airshed air quality model. The results of such a modeling exercise could in turn be compared to the results derived from the reactivity analysis presented above. It is suggested that simulations include sensitivity analysis based on an urban airshed model for both 1- and 8-hr peak ozone impacts.

DESCRIPTION:

The 2010 baseline emission inventory used for the 2003 South Coast SIP update will be used to investigate the effect on peak ozone concentration (1-hr and 8-hr) due to CO and VOC emissions from on-road vehicles. On-road CO emissions will be reduced by 10 percent to see the impact on peak ozone while in a separate simulation, the emissions of on-road vehicle exhaust VOC will be increased by 10 percent. (On-road vehicle exhaust VOC will be employed as a surrogate for permeation VOCs due to their similar composite MIR values).

The simulations will be conducted for a multiple-day ozone episode (August 3-7, 1997) using the CALGRID photochemical model with the SAPRC99 photochemical mechanism. Only on-road exhaust emissions from gasoline vehicles will be varied for these simulations since the diesel portions of CO and VOC are small. Below is a summary of the proposed tasks.

- The 2010 baseline 1-hr and 8-hr peak ozone modeling will be performed first. Modeling simulations with both CO reduction and permeation VOC increase will then be conducted and the resulting ozone difference from the baseline will be calculated. The effective 1-hr and 8-hr ozone impacts of VOCs relative to that of CO per ton of emission change can then be obtained and compared to those derived from the reactivity analysis.
- Population exposure for 1-hr ozone above a threshold of 125 ppb will be estimated for the above three scenarios. The ratio of VOC/CO one-hour population-weighted exposure impacts will be calculated. The same procedure will be applied to the ROG/CO 8-hour population-weighted exposure impact.
- If the modeling results in terms of ozone impact are not significant, refined modeling simulations including attainment conditions and permeation VOC profiles could be considered.

CONCLUSIONS

- Results from such a modeling exercise will be shared with interested stakeholders for review and comment.
- Results may also help to determine if modeling results are reasonably consistent with reactivity analyses in assessing the ozone impact of permeation VOCs relative to CO emissions.

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